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14. ABSTRACT The symposium consisted of eight invited speakers plus two contributed talks, over a one-day period. The talks included both theory and experiment, leading to an excellent exchange of ideas and possibly leading to new collaborative efforts.					
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FINAL CONFERENCE REPORT
ACS SYMPOSIUM ON THREE-DIMENSIONAL SILICON-OXYGEN CAGES
AWARD F49620-01-1-0483

MARK GORDON

Takako Kudo discussed possible mechanisms for the formation of polyhedral oligomeric silsesquioxanes (POSS), using *ab initio* quantum chemistry. The study included analyses of the initial hydrolysis of the starting silanes, subsequent condensation to disiloxanes, and further condensation to cyclic structures. The latter are the direct precursors to the POSS. Professor Kudo also considered substituent effects, the effects of aqueous solvent and the related compounds in which POSS are partially or completely substituted by Ti atoms. The calculations were performed with a range of methods, from Hartree-Fock to coupled cluster. Correlation effects are very large, but MP2 and coupled cluster calculations do not differ greatly. Adding solvent water molecules decreases the barrier heights for nearly all steps to zero. Except for the increase in the initial barrier when H is replaced by t-butyl in the POSS compounds, the substituent effects are small.

Ravi Pandey presented the results of density functional studies on the polymer to SiO₂ conversion process for H-silsesquioxanes (HSQ). Gas-fill and planarization on electronic circuits can be achieved by low-temperature processing of HSQ. Professor Pandey considered HSQ with cage sizes varying from 8 to 16, that while local DFT methods reproduce the structures reasonably well, they over-estimate the binding energies/silicon atom. The basic bonding picture does not change upon going from T₈ to T₁₆, but there is a large change in the HOMO-LUMO gap, and therefore the band structure along this sequence, due mainly to large changes in the LUMO. T₁₄ and T₁₆ show gaps that arise mainly from SiH contributions to the LUMO.

Michael Bowers discussed the application of the MALDI (matrix-assisted laser desorption ionization) and ESI (electrospray ionization) techniques to the study of POSS compounds. The Bowers group combines these experimental methods with molecular

mechanics computations to study ion mobilities and collision cross sections of R_nT_n cages, where R is either cyclohexyl (Cy) or vinyl (Vi). Agreement between experiment and theory for the cross sections is excellent. According to MALDI, the least compact structure is the most abundant. The calculations predict that the more compact structures have smaller cross sections.

Sharon Hammes-Schiffer discussed nuclear quantum effects in hydrogen transfer reactions in POSS formation. Instead of using the more standard approaches, in which the moving H atom is first treated classically, with subsequent corrections for tunneling to account for "corner cutting", the Hammes-Schiffer group directly calculate the nuclear quantum effects. To avoid computationally demanding grid-based calculations, they have developed an analytical approach that uses nuclear electronic orbitals (NEO). The method uses multi-configurational treatments of both the nuclear and electronic motions. This method was applied to the initial condensation reaction, for which it was discovered that a proper quantal treatment of nuclear motion can lower barrier heights by as much as 9 kcal/mol.

Ian Carmichael discussed a study on atomic H in silsesquioxane cages, using density functional theory calculations to predict hyperfine splittings. This is of interest, since H inside T_8 was reported in 1994. The predicted temperature dependence of the hyperfine coupling agrees with experiment, but it is too weak, probably because a rigid cage potential was used.

Jack Tossell the behavior of Ti atoms in aluminosilicate minerals and zeolite catalysts. The particular questions addressed were: What are the spectral signatures for different local Ti geometries? How are Si and O signatures altered the proximity of Ti? How are the reactivity and properties of Ti-O-Ti affected by the proximity of Si-O. The calculations were done by using both Hartree-Fock and density functional theory to predict the NMR shielding. It is predicted that the presence of Ti has little effect on the ^{29}Si shielding but a very large effect on the O shielding.

Mark Banaszak-Holl presented results on his group's study of adsorption of POSS compounds on the Si(100) surface using STM techniques. It is found that the POSS prefer to adsorb at one Si, rather than on an edge, with the cluster remaining largely intact. They have also studied adsorption onto gold surfaces. In this case they find that the clusters react rapidly with the gold surface, including H exchange with the surface. A novel SiH activation is also observed at ambient temperatures.

Hai-Lung Dai discussed the photochemistry of silsesquioxane thin films. They are studying spin-on glass materials using new low-temperature deposition methods and 193 nm light. They then study the surface morphology using atomic force microscopy (AFM). It is believed that the RSiO group absorbs the photon, giving rise to R and SiO radicals. An oxygen source is required for the photochemistry to go to completion. Stochastic simulations were used to study the kinetics. Diffusion of the photofragments through the solid matrix is observed, followed by secondary reactions.

Barry Farmer used molecular dynamics (MD) simulations based on molecular mechanics to study the glass transition temperature of POSS-containing polymers. The glass transition temperature is predicted to increase with the weight percent of POSS, from 0 to 60%. His group also studied the diffusion of gaseous oxygen molecules in the presence of POSS with sizes varying from T_8 to T_{14} . It is predicted that even the largest cage is too small to permit diffusion of small molecules through the POSS cages.

Baudilio Tejerina studied the energetics of both N_2 and O_2 molecules passing through the faces of POSS cages, ranging in size from T_8 to T_{12} , using both Hartree-Fock and second order perturbation theory (MP2) methods. Inserting these molecules into the cages is endothermic in all cases, but the endothermicity and barrier height are smaller for O_2 than for N_2 , and both the endothermicity and the barrier decrease substantially as the size of the cage is increased. Preliminary MP2 results suggest that insertion of O_2 into the T_{12} cage may be feasible.

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<input type="checkbox"/>	Sunday Morning	8:20 AM	Paper 18: Ab initio study of silsesquioxanes. T. Kudo, M. S. Gordon	McCormick Place South Room S404A, Level 4	PHYS	Paper
<input type="checkbox"/>	Sunday Morning	9:00 AM	Paper 19: First-principles study of silsesquioxanes. R. Pandey	McCormick Place South Room S404A, Level 4	PHYS	Paper
<input type="checkbox"/>	Sunday Morning	9:40 AM	Paper 20: Conformations of POSS monomers in the gas phase. M. T. Bowers	McCormick Place South Room S404A, Level 4	PHYS	Paper
<input type="checkbox"/>	Sunday Morning	10:40 AM	Paper 21: Nuclear quantum effects in hydrogen-transfer reactions for the synthesis of polyhedral oligomeric silsesquioxanes. S. Hammes-Schiffer, S. P. Webb, T. Jordanov	McCormick Place South Room S404A, Level 4	PHYS	Paper
<input type="checkbox"/>	Sunday Morning	11:20 AM	Paper 22: Atomic hydrogen in silsesquioxane cages: Results and hypotheses. I. Carmichael, R. M. Macrae, M. Paech	McCormick Place South Room S404A, Level 4	PHYS	Paper
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Abstract

PHYS 18

Ab initio study of silsesquioxanes

Takako Kudo, Department of Fundamental Studies, Faculty of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Japan, Fax: +81-277-40-1026, tkudo@sci.gunma-u.ac.jp, and Mark S. Gordon, Chemistry, Iowa State University

Polyhedral oligomeric silsesquioxanes (POSS) have generated considerable interest in both the experimental and theoretical communities because of their wide practical uses. Although there have been many studies of their structures and properties, very little is known about the mechanism(s) by which they form. The synthetic process has three steps; (i) the typical hydrolysis of trihalosilane ($RSiX_3$) to form the corresponding trihydroxysilane, (ii) the initial condensation of the trihydroxysilane, and (iii) additional condensations, ultimately building to POSS structures. For each step, we have investigated not only the direct reaction in gas phase but also the effects of various substituents, catalysts, dehydrating agent, and solvent waters, which play an important role for the reactions. We will present some of the results. Recently, various metal-substituted POSS are also interesting research target. Especially, the titanium POSS is expected to have the excellent catalytic activities with combination of POSS and titanium atom. So, we will report out recent study for the structures, stabilities, and reactivities of the Ti analogs of POSS (Ti-POSS).

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Abstract

PHYS 19

First principles study of silsesquioxanes

Ravi Pandey, Department of Physics, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931, Fax: 906-487-2933, pandey@mtu.edu

H-silsesquioxanes constitute an important class of resinous inorganic polymers. Their building block is the trifunctional monomer, $(\text{HSiO}_{3/2})$, designated as the T unit. The structure of the polymer is based on siloxane-containing cages that are formed from the building block unit.

In this talk, we will present the results of a theoretical study on the T_n cages with $n=4, 6, 8, 10, 12, 14$, and 16 with an aim to determine their electronic properties. Calculations were performed in the framework of density functional theory using the double numeric basis sets. The calculated total energies of the T_n cages show a clear preference of four- and five-member rings by the smaller cages and of four- and six-member rings by the larger cages. A detailed analysis of binding energy, energy for hydrolysis reaction, and fragmentation paths suggests the relative stability of T_8 , T_{10} and T_{12} cages. The (lone-pair) oxygen p-type atomic orbitals form the HOMO of the T_n cages while the terminal hydrogens associated with silicons appear to give rise an electronic state in the HOMO-LUMO gap for the larger cages.

In collaboration with Udo Pernisz, Kai-hua Xiang, Ruth Franco, and Anil Kandlam.

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Abstract

PHYS 20

Conformations of POSS monomers in the gas phase

Michael T. Bowers, Chemistry, U.C. Santa Barbara, Santa Barbara, CA 93106, Fax: 805-893-8703,
bowers@chem.ucsb.edu

Recently we have developed methods to determine conformations of macromolecular species in the solvent free gas phase. the method involves generation of singly charged species using MALDI or ESI and measuring the mobility of the mass selected species formed. Extensive computer modeling generates structures and cross sections of low energy species that can be compared with experiment. In this talk we will discuss recent results on a variety of POSS monomers capped with reagents varying from H-atoms to styrene. The utility of the method for aiding synthesis by providing relatively rapid analysis of product distributions and structures will be discussed.

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Abstract

PHYS 21

Nuclear quantum effects in hydrogen transfer reactions for the synthesis of polyhedral oligomeric silsesquioxanes

Sharon Hammes-Schiffer, Simon P. Webb, and Tzvetelin Jordanov, Department of Chemistry, Pennsylvania State University, 152 Davey Lab, University Park, PA 16802, Fax: 814-863-5319, shs@chem.psu.edu

A mixed electronic/nuclear molecular orbital method for the simultaneous calculation of electronic and nuclear wavefunctions will be presented. Both electronic and nuclear molecular orbitals are expressed as linear combinations of Gaussian basis functions, and the variational method is utilized to minimize the energy with respect to all molecular orbitals. The methodology has also been developed for the calculation of excited electronic and vibrational states. In addition, this approach may be combined with the generation of minimum energy paths and dynamic reaction paths. For hydrogen transfer reactions, the transferring hydrogen nuclei, as well as all electrons, are treated quantum mechanically to include nuclear quantum effects such as zero point energy and hydrogen tunneling. The application of this approach to hydrogen transfer reactions in the hydrolysis and condensation steps required for the synthesis of polyhedral oligomeric silsesquioxanes (POSS) will be presented. These calculations elucidate the role of nuclear quantum effects in the mechanism for the synthesis of POSS. Such mechanistic information is critical for the efficient synthesis of POSS and the production of new functional POSS species.

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Abstract

PHYS 22

Atomic hydrogen in silsesquioxane cages: Results and hypotheses

Ian Carmichael, Roderick M. Macrae, and Michael Pacch, Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, carmichael.1@nd.edu

Different silsesquioxanes comprising the cube shaped Si_8O_{12} -unit were found to stabilize radiolytically generated atomic hydrogen by entrapment under ambient conditions. This merely interesting fact becomes more surprising, if one takes a closer look at the conditions that promote the entrapment. Potent radical scavengers like iodine, oxygen and phenols as well as certain compounds, known as electron scavengers were found to drastically increase the yield of trapped hydrogen atoms. Certain amines were found to behave like trapping inhibitors. Experimental evidence is presented for radiation induced processes, which empty formerly filled cages. As there is no obvious direct way to measure the kinetic energy needed for an H atom to enter the cavity, an indirect approach was chosen: By carefully measuring the activation energy needed for thermal detrapping, an theoretically obtained energetic profile for the whole trapping process could be corroborated. This profile in turn yielded a guess of the range of kinetic energies favorable for hydrogens to be trapped. Isotope effects regarding kinetics and hyperfine couplings have been detected and are discussed.

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<input type="checkbox"/>	Sunday Afternoon	1:40 PM	Paper 40: Ti-containing silsesquioxanes: NMR properties and acidity. J. A. Tossell	McCormick Place South Room S404A, Level 4	PHYS	Paper
<input type="checkbox"/>	Sunday Afternoon	2:20 PM	Paper 41: Spherosiloxane cluster-based monolayers on gold and silicon surfaces. M. M. Banaszak Holl, K. Nicholson, K. Schneider	McCormick Place South Room S404A, Level 4	PHYS	Paper
<input type="checkbox"/>	Sunday Afternoon	3:00 PM	Paper 42: Photochemistry in thin silsesquioxane films. H-L. Dai	McCormick Place South Room S404A, Level 4	PHYS	Paper
<input type="checkbox"/>	Sunday Afternoon	4:00 PM	Paper 43: Molecular dynamics simulations of POSS-containing polymers. B. L. Farmer, R. J. Berry, R. K. Bharadwaj	McCormick Place South Room S404A, Level 4	PHYS	Paper
<input type="checkbox"/>	Sunday Afternoon	4:40 PM	Paper 44: Insertion mechanism of N ₂ and O ₂ into T _n (n = 8, 10, 12)-silsesquioxanes framework. B. L. Tejerina, M. S. Gordon	McCormick Place South Room S404A, Level 4	PHYS	Paper

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Abstract

PHYS 40

Ti-containing silsesquioxanes: NMR properties and acidity

John A. Tossell, Dept. of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, Fax: 301-314-9121, tossell@chem.umd.edu

Silsesquioxanes serve as model systems for silicate minerals and glasses. Previously we have studied trends in ^{29}Si NMR spectra, energetics of Al-Si distributions and the dependence of silicate acidity upon oligomerization using such models. In the present study, Ti-bearing silsesquioxanes and silicate models, such as the double-4-ring molecule $\text{Si}_4\text{Ti}_4\text{O}_{20}\text{H}_8$ have been treated using Hartree-Fock and density functional techniques. The NMR chemical shifts of Si, Ti, O and H have been calculated for different isomeric forms of $\text{Si}_4\text{Ti}_4\text{O}_{20}\text{H}_8$, some of which violate the Al-avoidance principle. We have also evaluated the acidity of H's in Si-O-H and Ti-O-H groups by calculating the gas phase deprotonation energy and estimating the hydration energy of the silsesquioxane anion. Visible-UV absorption energies have been calculated using both Hartree-Fock based configuration interaction singles and time dependent density functional theory. The use of partially depolymerized silsesquioxanes as models for study of the acidity and reactivity of silica surfaces will also be briefly discussed.

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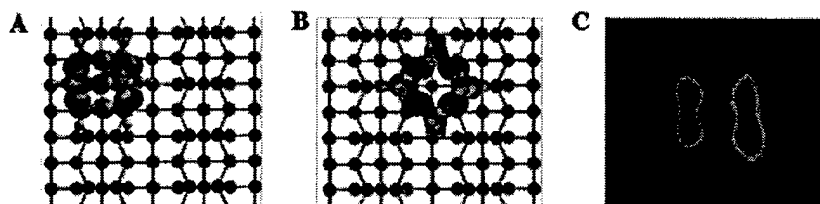
Abstract

PHYS 41

Spherosiloxane cluster-based monolayers on gold and silicon surfaces

Mark M. Banaszak Holl, Kenneth Nicholson, and Kevin Schneider, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, Fax: 734-763-2307, mbanasza@umich.edu

Hydrospherosiloxane clusters H₈Si₈O₁₂ and H₁₀Si₁₀O₁₅ react with gold and silicon surfaces via a vertex Si-H bond to form a chemisorbed monolayer. The preparation, spectroscopic characterization, and dynamic behavior of these cluster layers will be discussed. Characterization methods include X-ray Photoelectron Spectroscopy, Reflection-Absorption Infrared Spectroscopy, and Scanning Tunneling Microscopy. These models are relevant for understanding the hydrogen reactions occurring at the interfaces of Metal Oxide Semiconductor Field Effect Transistors (MOSFETs). The clusters also provide an interesting alternative to alkanethiol-based self-assembled monolayer technology. The STM image of an H₈Si₈O₁₂ cluster on Si(100) shown below gives a direct comparison of A) cracked-cluster and B) monovortex bonding models with the C) STM data using a constant color scheme and orientation.



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Abstract

PHYS 42

Photochemistry in thin silsesquioxane films

Hai-Lung Dai, Department of Chemistry, University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104, Fax: 215-898-2037, dai@sas.upenn.edu

Under UV (193 nm) radiation, thin films of β -chloroethyl silsesquioxane, spin coated on a variety of surfaces, convert to silicon dioxide. The deposited silicon oxide films are of high chemical purity and refractive index. Time-resolved Mass Spectrometry analysis of gaseous fragments emerging from the thin films during the irradiation reveals the photochemical mechanism. The 193 nm photon absorbed through the Si-R chromophore induces the dissociation of the Si-O bond. Si-O-Si cross linking occurs through reactions of the un-bonded Si atoms with nearby oxygen containing species. The R fragments diffuse through the solid film and react with Si-R groups on the way out into the gas phase. When the thin films are below several hundred angstroms in thickness, the R fragment diffusion has no effect in the silicon oxide formation rate. When the films are thicker, the diffusion and reaction of the R fragments in the solid substantially slow down the rate of conversion from silsesquioxane to silicon dioxide. Other aspects important to the understanding of photochemistry in thin solid films will also be discussed.

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Abstract

PHYS 43

Molecular dynamics simulations of POSS-containing polymers

B. L. Farmer¹, Rajiv J. Berry¹, and R. K. Bharadwaj². (1) Materials and Manufacturing Directorate (AFRL/MLBP), Air Force Research Laboratory, 2941 P. St., Suite 1, Wright-Patterson AFB, OH 45433, Fax: 937-255-9157, Barry.Farmer@afrl.af.mil, (2) Avery Research Center

Molecular dynamics simulations have been used to explore the effects of introducing polyhedral oligomeric silsesquioxane (POSS) moieties into polynorbornene as a tethered pendant group or as a molecular dispersant. POSS having isobutyl, cyclopentyl, or cyclohexyl substituents have been considered. The effects of the type of substituent and tethering vs. dispersing on the thermomechanical properties and on diffusion of oxygen have been examined. Tethered POSS moieties slow the segmental dynamics of the polymer, and thereby impart increased stiffness. Untethered POSS is less effective in enhancing the thermomechanical properties. The internal volume of the T8 POSS moiety is unavailable to diffusants and POSS therefore tends to enhance barrier properties of the composite material. The nature of the POSS substituents also impacts the diffusion rate for oxygen. Molecularly dispersed POSS moieties tend to be more effective in this regard than when the silica cage is tethered to the polymer chain.

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Abstract

PHYS 44

Insertion mechanism of N_2 and O_2 into T_n ($n=8, 10, 12$)-silsesquioxanes framework

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The interaction of small molecules, as N_2 or O_2 , with polyhedral oligomeric silsesquioxanes POSS- T_n cages (see figure 1 for $n=8$) can lead to the formation of clusters that hold such molecules in their interior (figure 3). The mechanism of insertion involves the pass of the small molecule through one of the faces of the polyhedron. This intermediate structure has been characterized as transition geometry between the POSS and the cluster (figure 2). The formation of the most stable cluster with N_2 (D_{2h}) implies an energetic increment of +142.27 kcal/mol⁻¹ while for the case of the cluster with O_2 , the geometry is D_{4h} and the variation of the energy in its formation is +116.97 kcal/mol⁻¹.

